Introduction of Isotope Ratio Mass Spectrometry (IRMS) for the Forensic Analysis of Explosives

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CERTIFICATE OF AUTHORSHIP/ORIGINALITY

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Signature

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SYMBOLS

δ	Delta value
‰	Parts per thousand = per mill = 10^{-3}
s	Standard deviation
X	Assigned value
σ	Standard deviation for proficiency assessment
u_X	Standard uncertainty of the assigned value

ABBREVIATIONS

AFP	Australian Federal Police
AN	Ammonium Nitrate
ANFO	Ammonium Nitrate/Fuel Oil
BSIA	Bulk Stable Isotope Analysis
C	Carbon element
CE	Capillary Electrophoresis
CF-IRMS	Continuous Flow Isotope Ratio Mass Spectrometry
CI	Confidence Interval
CO	Carbon Monoxide gas
CO_2	Carbon Dioxide gas
COAG	Council of Australian Governments
CRM	Certified Reference Material
CSIA	Compound Specific Isotope Analysis
DADP	Diacetone diperoxide
DI-IRMS	Dual Inlet Isotope Ratio Mass Spectrometry
EA/IRMS	Elemental Analysis Isotope Ratio Mass Spectrometry
FC	Faraday Cup
FEL	The Forensic Explosives Laboratory (FEL), Defence Science and Technology Laboratory (DSTL), United Kingdom (UK)
FIRMS	Forensic Isotope Ratio Mass Spectrometry Network
FTIR	Fourier Transform Infrared Spectrometry
GC	Gas Chromatography
GC/ECD	Gas Chromatograph - Electron Capture Detector
GC/FID	Gas Chromatograph - Flame Ionisation Detector
GC/IRMS	Gas Chromatography - Isotope Ratio Mass Spectrometry
GC/MS	Gas Chromatograph - Mass Spectrometer
GC/TEA	Gas Chromatograph - Thermal Energy Analyser
H	Hydrogen element
H_2	Hydrogen gas
HMTD	Hexamethylene triperoxide diamine
HMX	Cyclotetramethylene tetranitramine
HPLC	High Performance Liquid Chromatography
HTP	High Temperature Pyrolysis
IAEA	International Atomic Energy Agency, Vienna Austria

IC	Ion Chromatography
IED	Improvised Explosive Device
IRA	Irish Republican Army
IRMS	Isotope Ratio Mass Spectrometry
KT	Kaltenbach-Thuring
LC/MS	Liquid Chromatography/Mass Spectrometry
MDMA	Methylenedioxymethylamphetamine
MU	Measurement Uncertainty
N	Nitrogen element
N_2	Nitrogen gas
NATA	National Association of Testing Authorities, Australia
NG	Nitroglycerine
NIST	National Institute of Standards and Technology, Washington DC USA
O	Oxygen element
O_2	Oxygen gas
PDB	PeeDee Belemnite
PETN	Pentaerythritoltetranitrate
QC	Quality Control
RDX	Cyclotrimethylene trinitramine
RSD	Relative Standard Deviation
SEM/EDX	Scanning Electron Microscopy Energy Dispersive X-Ray Spectroscopy
SSAN	Security Sensitive Ammonium Nitrate
TATB	Triaminotrinitrobenzene
TATP	Triacetone triperoxide
TC/EA	High Temperature Conversion Elemental Analyser
TNT	Trinitrotoluene
VSMOW	Vienna Standard Mean Ocean Water
XRD	X-ray Diffraction
XRF	X-ray Fluorescence Spectrometry

Abstract

The key role of a forensic scientist is to assist in determining whether a crime has been committed and, if so, assist in the identification of the offender. It is a commonly held belief that a particular item can be conclusively linked to a specific person, place or object. Unfortunately, this is often not an achievable outcome.

An evaluation was undertaken to determine if isotope ratio mass spectrometry (IRMS) could assist in the investigation of complex forensic cases by providing a level of discrimination not achievable utilising traditional forensic techniques. The focus of the research was on ammonium nitrate (AN), a common oxidiser used in improvised explosive mixtures. A secondary objective was to adapt the methods and protocols developed for AN for the analysis of other threat explosives, namely triacetone triperoxide (TATP) and pentaerythritol tetranitrate (PETN).

The potential of IRMS was demonstrated through the successful development and validation of a method for the measurement of bulk nitrogen isotope ratios in AN samples and the subsequent development of an AN classification scheme based on nitrogen stable isotopes to assist in determining the potential manufacturer (in the case of an Australian source). Although the discrimination was limited, the classification scheme could be used as an investigative aid.

A comparison of nitrogen isotope ratios from intact AN prill samples with those from post-blast AN prill residues highlighted that the nitrogen isotopic composition of the prills is not maintained; hence, this is a limitation of the technique for explosives analysis.

Combining oxygen and hydrogen stable isotope ratios permitted the differentiation of AN prills from three different Australian manufacturers. Groups corresponding to source were also identified in the overseas AN prill samples. When these values were combined with the nitrogen isotope values, there was some level of discrimination

(within the scope of the samples analysed) between prills manufactured in Australia and those manufactured overseas.

The IRMS procedures developed through this research were successfully applied to the analysis of both TATP and PETN. Preliminary results of a limited sample set demonstrated that TATP sources may be discriminated utilising carbon and hydrogen isotopes alone, and in combination with oxygen isotopes. Preliminary results for PETN samples demonstrated that different sources can be discriminated based on carbon and nitrogen isotope ratios.

A laboratory inter-comparison for carbon and nitrogen bulk stable isotope ratios across seven Australian and New Zealand IRMS laboratories was conducted and provides an initial snapshot of the potential for traceability. A Microsoft Access 2.0 database was developed for the IRMS data and its successful operation demonstrated.

This research highlights the significant value of IRMS in complex forensic investigations, particularly with respect to explosives analysis. Further research is justified to continue the path towards broader forensic casework application of the technique.